

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
23 August 2001 (23.08.2001)

PCT

(10) International Publication Number  
WO 01/60959 A1

(51) International Patent Classification<sup>7</sup>: C10M 169/04,  
159/18 // C10N 10:12, 30:04, 30:06, 30:10, 40:25

Samia, Ontario N7S 4A7 (CA). TORKELSON, Jeffrey,  
Robert [CA/US]; Mont Laurel, NJ 08801 (US). WOOL-  
LEY, Paul, S. [GB/GB]; 33 Equine Way, Newbury,  
Berkshire RG14 7XB (GB).

(21) International Application Number: PCT/US01/09730

(22) International Filing Date: 8 February 2001 (08.02.2001)

(74) Agent: MULLER, W., G.; ExxonMobil Chemical Europe  
Inc., P.O. Box 105, B-1830 Machelen (BE).

(25) Filing Language: English

(81) Designated States (*national*): AU, BR, CA, JP, SG, US.

(26) Publication Language: English

(30) Priority Data:  
0003388.6 14 February 2000 (14.02.2000) GB

(84) Designated States (*regional*): European patent (AT, BE,  
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,  
NL, PT, SE, TR).

(71) Applicant (*for all designated States except US*): EXXON-  
MOBIL RESEARCH AND ENGINEERING COM-  
PANY [US/US]; 1545 Route 22 East, Clinton Township,  
Annandale, NJ 08801 (US).

**Published:**

- with international search report
- before the expiration of the time limit for amending the  
claims and to be republished in the event of receipt of  
amendments

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): GAO, Jason  
[CA/US]; 535 Walnut Lane, Swarthmore, PA 19081 (US).  
MAY, Christopher, John [CA/CA]; 1571 Bove Court,

*For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.*



WO 01/60959 A1

(54) Title: LUBRICATING OIL COMPOSITIONS

(57) Abstract: This invention relates to a lubricating oil composition comprising a base stock and an antioxidant comprising an oil soluble trinuclear organomolybdenum compound of the generic formula (I):  $\text{Mo}_3\text{S}_x\text{-(Q)}$  wherein x is from 4 to 10 and Q is a core group, which may be a ligand, and at least one other compound selected from a phenolic and an aminic compound wherein the basestock has a kinematic viscosity at 100 °C ( $\text{KV}_{100}$ ) from about 2 cSt to 20 eSt ( $2 \times 10^{-6}$  to  $20 \times 10^{-6} \text{ m}^2/\text{sec}$ ) and a saturates content of at least 85 %. The composition has a high oxidation stability, reduced deposit formation and is capable of giving rise to a good fuel economy improvement.

## LUBRICATING OIL COMPOSITIONS

This invention relates to lubricating oil compositions, especially lubricants used in internal combustion engines, comprising base oils high in saturates which are resistant to oxidation.

Lubricating oil compositions are used for the smooth operation of internal combustion engines, power transmission components including automatic transmissions, shock absorbers and power steering devices and gears. The engine oils for internal combustion engines in particular serve to (i) lubricate various sliding interfaces eg between the piston ring and cylinder liner, in bearings of the crank shaft and the connecting rod, and in the valve driving mechanism including cams and valve lifters, (ii) cool the engine, (iii) clean and disperse the combustion products and (iv) prevent corrosion and consequent rust formation. The stringent requirements for high performance engines in recent years has meant greater demand from lubricants used in such engines. Lubricating oils used in such engines usually deteriorate due to oxidation by oxygen and nitrogen oxides (NOx) formed during combustion of fuels and lubricants and that contained in blow-by gas in turn formed by leakage of combustion gases into the crankcase via the piston and cylinder interface. The concentration of NOx increases in the blow-by gas with increasing demand in performance of the engine. The deleterious effects of oxidation can be and have been mitigated by the use of various additives including antioxidants, anti-wear agents, ash-free detergent dispersants, friction modifiers and the like.

Hitherto these have been mitigated to some extent by the use of lubricating compositions which comprise a Group I base oil which is relatively low in saturated hydrocarbons (hereafter "saturates") in spite of its relatively high propensity to oxidation. Whilst this has meant that the base oil itself is relatively inexpensive, it has had to be supplemented with relatively large amounts of additives/antioxidants to achieve the desired performance. However, by using a relatively more refined feedstock such as the Group II & Group III basestocks high in saturates, it is possible to achieve the desired performance without unduly supplementing the additives/antioxidants used.

It has now been found that by using a specific combination of antioxidants, it is possible to use Group II and Group III base stocks high in saturates with enhanced performance in respect of oxidation stability and fuel efficiency.

Accordingly, the present invention is a lubricating oil composition comprising a base stock and an antioxidant comprising an oil soluble trinuclear organomolybdenum compound of the generic formula:



wherein x is from 4 to 10, preferably 7, and Q is a core group, which may be a ligand, and at least one other compound selected from a phenolic and an aminic compound characterised in that the base stock has a kinematic viscosity at 100°C (KV<sub>100</sub>) from about 2 cSt to 20 cSt (2 x 10<sup>-6</sup> to 20 x 10<sup>-6</sup> m<sup>2</sup>/sec) and a saturates content of at least 85%.

The lubricating oil compositions of the present invention are those that comprise a major amount of a Group II or Group III base stock which may be a natural or synthetic lubricating oil having a KV<sub>100</sub> of 2-20 cSt, preferably from 2-12 cSt and a saturates content of at least 85%, preferably at least 88%. Specific examples of Group II basestock high in saturates include *inter alia* RLOP 500R and Mobil Jurong 500N (with > 97% saturates), and MXT 5 (with 92% saturates); and examples of Group III basestock include *inter alia* Yubase 4 (with saturate contents of 99.5%) and Yubase 6 (with saturate contents of 97.5%).

According to a further embodiment, the present invention is a method of stabilizing a lubricant composition against oxidative degradation, said composition comprising a base stock which has a kinematic viscosity at 100°C (KV<sub>100</sub>) from about 2 cSt to 20 cSt (2 x 10<sup>-6</sup> to 20 x 10<sup>-6</sup> m<sup>2</sup>/sec) and a saturates content of at least 85% said method comprising adding to the basestock an effective amount of an antioxidant comprising an oil soluble trinuclear organomolybdenum compound of the generic formula:



wherein x is from 4 to 10, preferably 7, and Q is a core group, which may be a ligand, and at least one other compound selected from a phenolic and an aminic compound.

The trinuclear molybdenum compounds are of formula (I)



wherein x is from 4 to 10, preferably 7, and Q is a core group. These compounds are relatively new and are claimed and described in our prior published US-A-5,906,968. The matter disclosed in this prior US patent on the structure, preparation and properties of the trinuclear molybdenum compounds is incorporated herein by reference. In these compounds the core group (Q) may be a ligand capable of rendering the organomolybdenum compound of formula (I) oil soluble and ensuring that said molybdenum compound is substantially charge neutral. The core group (Q) is generally associated with suitable ligands such as L<sub>y</sub> wherein L is the ligand and y is of a sufficient number, type and charge to render the compound of formula (I) oil soluble and to neutralise the charge on the compound of formula (I) as a whole. Thus, more specifically, the trinuclear molybdenum compound used in the compositions of the present invention may be represented by the formula (II):



The ligands "L" are suitably dihydrocarbyl dithiocarbamates of the structure (-S<sub>2</sub>CNR<sub>2</sub>) wherein the dihydrocarbyl groups, R<sub>2</sub> impart oil solubility to the molybdenum compound. In this instance, the term "hydrocarbyl" denotes a substituent having carbon atoms directly attached to the remainder of the ligand and is predominantly hydrocarbyl in character within the context of this invention. Such substituents include the following:

- (1) hydrocarbon substituents, ie, aliphatic (for example alkyl or alkenyl), alicyclic (for example cycloalkyl or cycloalkenyl), aromatic-, aliphatic- and alicyclic-substituted aromatic nuclei and the like, as well as cyclic substituents wherein the ring is completed through another portion of the ligand (that is, any two indicated substituents may together form an alicyclic group);
- (2) substituted hydrocarbon substituents, ie, those containing nonhydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbyl character of the substituent. Those skilled in the art will be aware of suitable groups (eg halo (especially chloro), amino, alkoxyl, mercapto, alkylmercapto, nitro, nitroso, sulphoxy etc.); and
- (3) hetero substituents, ie, substituents which, while predominantly hydrocarbon in character within the context of this invention, contain atoms other than carbon present in a chain or ring otherwise composed of carbon atoms.

The hydrocarbyl groups are preferably alkyl (e.g, in which the carbon atom attached to the remainder of the ligand "L" is primary, secondary or tertiary), aryl, substituted aryl and/or ether groups.

Importantly, the hydrocarbyl groups of the ligands should be such that they have a sufficient number of carbon atoms to render the compound (I) soluble or dispersible in the oil to which the trinuclear organomolybdenum compound containing the ligand is added. The total number of carbon atoms present among all of the hydrocarbyl groups of the organomolybdenum compounds' ligands is suitably at least 21, preferably at least 25, more preferably at least 30 and even more preferably at least 35, typically e.g., 21 to 800. For instance, the number of carbon atoms in each hydrocarbyl group will generally range from 1 to 100, preferably from 1 to 40 and more preferably from 3 to 20.

The antioxidant in the compositions of the present invention suitably also include at least one other compound selected from a phenolic compound and an aminic compound. Among the phenolic compounds, hindered phenols are preferred.

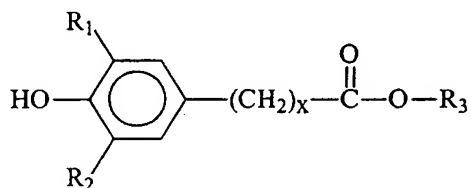
Examples of such phenolic compounds include *inter alia*:

- 4,4'-methylene bis(2,6-di-tert-butylphenol)  
 4,4'-bis(2,6-di-tert-butylphenol)  
 5 4,4'-bis(2-methyl-6-tert-butylphenol)  
 2,2'-methylene bis(4-ethyl-6-tert-butylphenol)  
 2,2'-methylene bis(4-methyl-6-tert-butylphenol)  
 4,4'-butylidene bis(3-methyl-6-tert-butylphenol)  
 4,4'-isopropylidene bis(2,6-di-tert-butylphenol)  
 10 2,2'-methylene bis(4-methyl-6-nonylphenol)  
 2,2'-isobutylidene bis(4,6-dimethyl phenol)  
 2,2'-methylene bis(4-methyl-6-cyclohexylphenol)  
 2,6-di-tert-butyl-4-methylphenol  
 2,6-di-tert-butyl-4-ethylphenol and  
 15 2,4-dimethyl-6-tert-butylphenol

Specific hindered phenols which are preferred as the antioxidants may be represented by the generic formulae (III) - (IV) below in which  $R_1$ ,  $R_2$ , and  $R_3$  are the same or different alkyl groups from 3-9 carbon atoms and  $x$  and  $y$  are integers from 1 to 4.

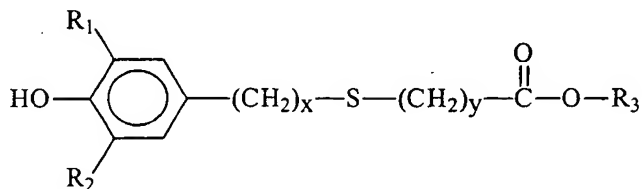
20

(III)



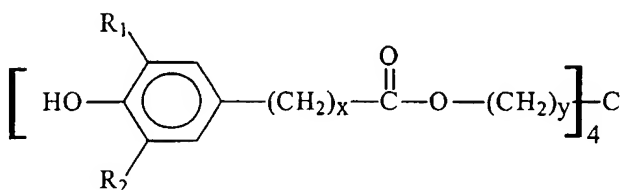
25

(IV)

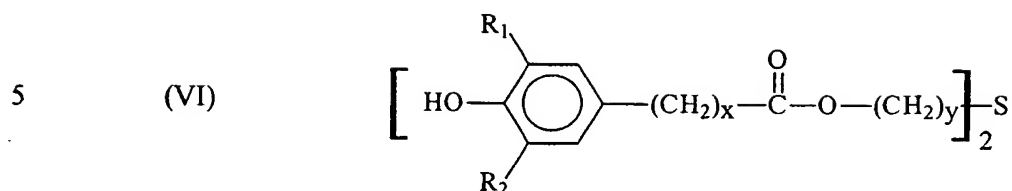


30

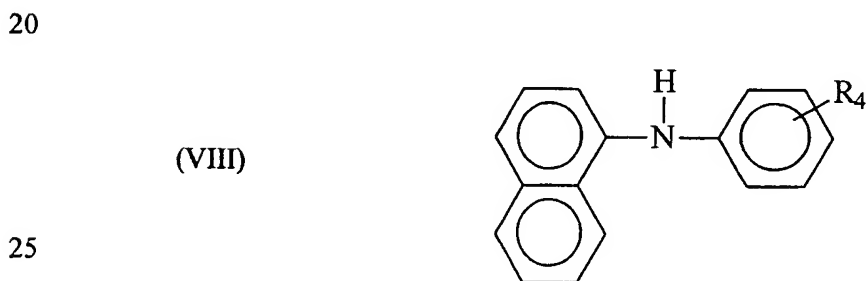
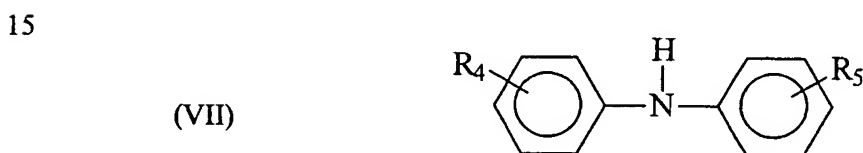
(V)



35



Suitable aminic compounds for use in the compositions of the present invention are diaryl amines, aryl naphthyl amines and alkyl derivatives of diaryl amines and the aryl  
 10 naphthyl amines. Preferred aminic antioxidants are represented by the formulae (VII) and (VIII) wherein each of  $R_4$  and  $R_5$  is a hydrogen atom or represents the same or different alkyl groups from 1-8 carbon atoms.



Specific examples of the aminic compounds that may be used in the compositions of the present invention include *inter alia*:

30

Monoalkyldiphenyl amines such as eg monooctyldiphenyl amine and monononyl diphenyl amine; dialkyldiphenyl amines such as eg 4,4'-dibutyldiphenyl amine, 4,4'-dipentyldiphenyl amine, 4,4'-dihexyldiphenyl amine, 4,4'-diheptyldiphenyl amine, 4,4'-dioctyldiphenyl amine and 4,4'-dinonyldiphenyl amine; polyalkyldiphenyl amines such as eg  
 35 tetra-butyldiphenyl amine, tetra-hexyldiphenyl amine, tetra-octyldiphenyl amine and tetra-nonyldiphenyl amine; the naphthylamines such as eg  $\alpha$ -naphthylamine and phenyl- $\alpha$ -naphthylamine; butylphenyl- $\alpha$ -naphthylamine, pentylphenyl- $\alpha$ -naphthylamine, hexylphenyl- $\alpha$ -naphthylamine, heptylphenyl- $\alpha$ -naphthylamine, octylphenyl- $\alpha$ -naphthylamine and

nonylphenyl- $\alpha$ -naphthylamine. Of these, dialkyldiphenyl amine and naphthylamines are preferable.

5 In general, the antioxidant which comprises the organomolybdenum compound in combination with a phenolic and/or an aminic compound will form a minor component of the total lubricant composition. For example, the organomolybdenum compound typically will comprise about 0.05 to about 5.00 wt % of the total composition, preferably from 0.05 to 2.0 wt%, and more preferably from 0.1 to 0.7 wt%, i.e., the molybdenum metal is suitably present in an amount of from about 25 to 2500 ppm, preferably from about 50 to 1000 ppm, 10 and more preferably from 100 to 700 ppm, and the phenolic and/or aminic compounds about 0.10 to about 3.0 wt % of the total composition.

It has also been found that if the weight ratio of organomolybdenum compound to the phenolic and/or aminic compound in the antioxidant is in the range of about 80:20 to about 20:80, optimum dispersancy retention can be achieved by these combined antioxidants of the 15 present invention.

It is particularly preferred that the antioxidant comprises in addition to the organomolybdenum compound, a mixture of the phenols (III)-(VI) above and the diaryl amines (VII)-(VIII) in a weight ratio ranging from about 80:10:10 to about 10:30:60 respectively, 20 preferably typically 50:15:35 respectively.

Optionally, the antioxidants may be combined with a carrier liquid in the form of a concentrate. The concentration of the combined antioxidants in the concentrate may vary 25 from 1 to 80% by weight, and will preferably be in the range of 5 to 50% by weight.

The antioxidant combination of the present invention can be used with any of the conventional dispersants used hitherto in the lubricating compositions. Examples of such dispersants include *inter alia* the polyalkylene succinimides, Mannich condensation products 30 of polyalkylphenol-formaldehyde polyamine and boronated derivatives thereof. However, it is preferable to use ashless dispersants such as the ashless succinimides, especially the polyisobutenyl succinimides of a polyamine such as eg tetraethylenepentamine or its homologues, benzylamine ashless dispersants, and ester ashless dispersants. The dispersants are generally used in the compositions of the present invention in an amount ranging from 35 about 2-10% by weight based on the total weight of the lubricant composition, preferably from about 4-8% by weight.

A feature of the present invention is that the compositions of the present invention the presence of a trinuclear organo molybdenum compound facilitates the control of deposit formation from engine oils. More specifically, formulations containing eg a contribution of 200- 750 ppm, preferably from 450-550 ppm of Mo metal from the trimer and an additional  
5 contribution of from 80-100 ppm from a detergent inhibitor package enables the amount of deposit formed to be significantly reduced. Adverse effects, if any, due the presence of such molybdenum compounds in the formulation, eg copper strip corrosion, are readily mitigated by including in the formulation a corrosion inhibitor or a metal passivator. This reduction in deposit formation has been monitored by the so-called TEOST-MHT-2 test which test is  
10 similar to the conventionally used TEOST-33 test method except that it is run at a relatively lower temperature and for a longer time. These tests are especially designed to test the formulations for a GF-3 specification. The TEOST-33 test is carried out at temperature cycles which fluctuate from 200-500°C and last for about 2 hours and results in bulk oxidation of the oil (about 100 g). In contrast, the TEOST-MHT-2 test relates to high  
15 temperature engine deposits as measured in tests such as TU3HT and is carried out at about 285°C over 24 hours and is a thin-film test on about 8 g of oil. The TEOST-MHT-2 test measures deposits produced on a heated rod or in the oil itself (filtered residue) and the GF-3 specification is envisioned to specify a limit of 40 mg deposit. From the results in the Examples below it will be seen that the presence of a trinuclear organo molybdenum  
20 compound in such oils results in about 66% reduction in the total weight of the deposits formed which satisfies the GF-3 specification.

In general, these lubricating compositions may include additives commonly used in lubricating oils especially crankcase lubricants, such as antiwear agents, detergents,  
25 dispersants, rust inhibitors, viscosity index improvers, extreme-pressure agents, friction modifiers, corrosion inhibitors, emulsifying aids, pour point depressants, anti-foams and the like.

A feature of the present invention is that lubricant compositions comprising high  
30 saturates base oils and trinuclear organomolybdenum compounds in combination with a phenolic and/or an aminic compound as antioxidant provide unexpected improvement in oxidation control and significant benefits in fuel economy. In the case of lubricants compositions comprising high saturates base oils for diesel engine oils, the present invention confers the added benefits of viscosity increase control and dispersancy retention over  
35 compositions which contain only one of these antioxidants used alone.

The present invention is further illustrated with reference to the following Examples:



**EXAMPLES****General Procedure:**

5

A series of Test oils were prepared. These oils were then tested in a bench oxidation test which was conducted at 165°C under a mixed nitrogen/air flow, with 40 ppm iron from added ferric acetylacetonate as catalyst. The flow rates of air and nitrogen were controlled at 500 ml/min and 350ml/min respectively.

10

In these tests the following commercial materials have been used:

	Irganox® L57	is an octylated/butylated diphenylamine (ex Ciba Geigy)
	Irganox® L101	is a high molecular weight phenolic antioxidant (ex Ciba Geigy)
15	Irganox® L115	and Irganox® L 1035 are high molecular weight phenolic antioxidants with a thioether group (ex Ciba Geigy)
	Irganox® L06	is an alkylated phenyl- $\alpha$ -naphthylamine (ex Ciba Geigy)
	Irganox® L135	is a high molecular weight phenolic antioxidant (ex Ciba Geigy)
	Irganox® L150	is a mixture of alkylated diphenylamine, a phenolic antioxidant
20		and a phenolic antioxidant with a thioether group (ex Ciba Geigy)
	Paranox® 106	is a polyisobutenylsuccinimide dispersant (ex Infernum, Linden, NJ)
	Molyvan® 822	is a dinuclear molybdenum dithiocarbamate containing 5 % wt molybdenum (ex R T Vanderbilt Co)
25	PDN5203	is an experimental sample of trinuclear molybdenum dithiocarbamate containing 5% wt molybdenum
	Paratone 8451	is a viscosity index improver (ex Oronite)
	Paraflow®390	is a pour point depressant (ex Oronite)
	DI	is a conventional detergent inhibitor package which is free of a
30		friction modifier package
	120X	is a Group II base oil with > 92% in saturates (ex Imperial Oil, Canada)

The same conventional DI package was used in all the Examples and tests, where indicated.

35

**Examples A-I****Comparison between low and high saturates base oils:**

- 5 The compositions of the test oils in these used in these Examples and their changes in respective viscosities after a 48 hour oxidation test are given in Table 1 below:

**TABLE 1**

Example	A	B	C	D	E	F	G	H	I
MCT 30 (% wt)	93.0	93.0	93.0	-	-	-	-	-	-
RLOP 500R (% wt)	-	-	-	93.0	93.0	93.0	-	-	-
Mobil Jurong 500N (%wt)	-	-	-	-	-	-	93.0	93.0	93.0
Paranox®106 (% wt)	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Mo <sub>3</sub> -dithiocarbamate*	1.0	-	0.5	1.0	-	0.5	1.0	-	0.5
Irganox® L57	-	1.0	0.5	-	1.0	0.5	-	1.0	0.5
Fresh Oil KV <sub>100</sub> , cSt	12.99	13.18	13.06	12.87	12.64	<b>12.78</b>	12.6	12.31	<b>12.38</b>
Used Oil KV <sub>100</sub> , cSt	14.3	21.66	15.54	25.03	28.76	<b>12.87</b>	46.25	34.6	<b>12.59</b>
% Increase**	10.08	64.34	3.68	94.48	127.53	<b>0.70</b>	267.06	181.1	<b>1.70</b>

- 10 \* containing 11.5% wt of molybdenum  
 \*\*changes in viscosity after 48 hr oxidation tests.

- 15 From the above it can be seen that the trinuclear molybdenum dithiocarbamate and the diarylamine individually perform better in low saturates base oil, but, unexpectedly, a combination of the two gives a better performance in high saturates base oils than the individual components.

**EXAMPLES J-Q**

- 20 **Comparison between a trinuclear molybdenum compound and a dinuclear molybdenum compound**

The compositions of the test oils in Examples J-Q and their respective changes in viscosity data after a 48-hour oxidation test on each are shown in Table 2 below:

**TABLE 2**

Example	J	K	L	M	N	O	P	Q
MCT 30 (% wt)	93.0	93.0	93.0	93.0	-	-	-	-
RLOP 500R (% wt)	-	-	-	-	93.0	93.0	93.0	93.0
Paranox®106 (% wt)	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
PDN 5203 (wt%)*	1.0	-	0.5	-	1.0	-	0.5	-
Molyvan®822 (wt%)	-	1.0	-	0.5	-	1.0	-	0.5
Irganox® L57 (wt%)	-	-	0.5	0.5	-	-	0.5	0.5
Fresh Oil KV <sub>100</sub> , cSt	12.98	13.00	12.91	12.97	12.65	12.71	12.64	12.63
Used Oil KV <sub>100</sub> , cSt	16.19	24.94	13.59	13.93	78.99	79.50	12.77	12.87
% Increase*	24.7	91.8	5.3	7.4	524	526	1.0	1.9

\*changes in viscosity after 48 hr oxidation tests.

- 5 Examples J-Q show that the trinuclear molybdenum dithiocarbamate gives better performance than conventional dinuclear molybdenum dithiocarbamate in oxidation control. The performance of the trinuclear molybdenum compound is further enhanced in base oils high in saturates.

- 10 Synergy of Trinuclear Molybdenum Dithiocarbamate with a Base Oil High in Saturates in the presence of Antioxidant Mixtures:

#### Examples R-U

- 15 The changes in viscosity after a 32 hour oxidation test in Examples R-U is shown in Table 3 below:

**TABLE 3**

Example	R	S	T	U
MCT 30 (% wt)	93.0	93.0	-	-
RLOP 500R (% wt)	-	-	93.0	93.0
Paranox®106 (% wt)	6.0	6.0	6.0	6.0
Mo <sub>3</sub> -dithiocarbamate* (% wt)	0.5	0.5	0.5	0.5
Irganox® L57	0.5	-	0.5	-
Irganox®L150 (%wt)	-	0.5	-	0.5
Fresh Oil KV <sub>100</sub> , cSt	13.39	13.41	12.73	12.78
Used Oil KV <sub>100</sub> , cSt	13.64	13.62	12.78	12.82
% Increase**	1.87	1.57	0.39	0.31

\*containing 11.5% by wt molybdenum

\*\*changes in viscosity after 48 hr oxidation tests.

5

Examples R-U demonstrate that mixtures of aminic and phenolic antioxidants give equivalent performance to an aminic antioxidant. Base oils high in saturates provide additional benefit in viscosity control.

#### 10 Fuel Economy Improvement:

Fuel economy is measured in different types of engine tests including the Sequence VIA, Sequence VIB and the M111 tests. Sequence VIA and the M111 tests evaluate initial fuel economy while Sequence VIB test determines initial and retained fuel economy after 96 hours.

15 In all engine tests, fuel economy is estimated as a function of the hydrodynamic and boundary contribution of the lubricant to fuel consumption. The lubricant contribution under hydrodynamic conditions is mostly governed by the lubricant viscometrics under both low and high shear conditions while the lubricant contributions under boundary conditions are most governed by the friction modifier technology.

20 For the purpose of illustrating this invention, we concentrate on the lubricant contribution to the boundary operating range of the engine, which in the Sequence VIB test is measured in Stage 5 of that test whereas the Sequence VIA is measured in Stage 1 of that test. The following Examples, therefore, refer to test performances in Stage 1, Stage 5 and the M111 tests as appropriate.

25

**Example V:**

A 5W-20 formulation comprising a Group II base oil is shown in Table 4 below:

**TABLE 4**

5

Component	Weight %	Component type
MXT 5	79.034	Group II basestock
Paratone®8452*	6.10	OCP VI Improver
Parabar®9230**	10.50	Borated PIBSA-PAM dispersant
SAP 001**	2.25	Ca salicylate - 165 TBN
SAP007**	0.56	Mg salicylate - 345 TBN
Irganox®L135	0.30	High M W phenolic AOX
Parabar®9417**	0.36	Secondary ZnDDP
Paranox®15**	0.69	Primary ZnDDP
Parabar®10100**	0.20	Corrosion Inhibitor
Parabar®9499**	0.006	Demulsifier

\* Paratone®8452 is sold by Oronite, Richmond, California, USA

\*\* Parabar®, Paranox® and SAP additives are sold by Infenium, Linden, New Jersey, USA.

The fuel economy and fuel economy retention data were collected using a gasoline passenger car M111 fuel economy test (CES-L54-X-94) and a M111 fuel economy retention test. In the M111 fuel economy retention test, the duration of the test is extended by repeating the standard test cycles 21 times. Each test cycle is followed by a period of steady state aging. The aging is equivalent to 500 miles. The total test is thus equivalent to about 10,000 miles, and takes about 185 hours. Fuel consumptions are measured at every cycle, hence every 500 miles. The fuel consumption reference RL191 is measured both at the beginning and end of the test, thereby allowing uninterrupted aging of the test oil. The effects of a trinuclear molybdenum dithiocarbamate on fuel economy and fuel economy retention are shown in Table 5 below. The initial fuel economy improvement data are thus based on comparison with the industry reference oil RL191 (which is a 15W-40 engine oil).

20

**TABLE 5**

Formulation	Initial Fuel Economy / %	Integrated fuel economy improvement (vs base case) over 10,000 mile drain interval / %
Base case 5W-20 (Table 4)	2.20	-
Base case + 1.1% Sakaralube®155*	2.38	10.6
Base case + 0.2% PDN5203	2.54	34.6
Base case + 1.0% PDN 5203	2.73	36.2

\*Sakaralube®155 is a dinuclear Mo dithiocarbamate (5% wt Mo, ex Asahi Denko Kogyo KK)

- 5 Example V shows that addition of molybdenum compounds leads to better fuel economy retention in a European gasoline passenger car engine. The use of trinuclear molybdenum dithiocarbamate provides significant improvement in initial fuel economy and fuel economy retention over the conventional dinuclear molybdenum dithiocarbamate.

10 **Example W:**

A 5W-20 engine oil formulation comprising a Group III base oil is shown in Table 6 below:

**TABLE 6**

15

Component	Weight %	Component type
Yubase 6	45.4	Group III basestock
Yuabse 4	40.3	Group III basestock
DI	8.3	DI package free of friction modifier
Paratone®8464*	6.10	OCP VI Improver

\* Paratone®8464 is sold by Oronite, Richmond, California, USA

- 20 The sequence VIA screener data in stages 1, 4 and 7 (stages sensitive to friction modifier) using a trinuclear molybdenum dithiocarbamate on fuel economy are shown in Table 7. The % fuel economy improvement was measured versus an industry baseline calibration oil (BC-3) for Sequence VIA (BC-3 is a non-friction modified synthetic 5W-30).

**TABLE 7**

Formulation	% Fuel Economy Improvement		
	Stage 1	Stage 4	Stage 7
Base case (Table 6)	0.612	1.804	-0.622
Base case + 1.0% PDN 5203	2.214	1.998	0.854

Thus, Example W further demonstrates the benefit of trinuclear molybdenum  
 5 dithiocarbamate in fuel economy improvement in a North American gasoline engine.

**EXAMPLE X:**

The TEOST-MHT-2 test was performed in a manner very similar to the conventional  
 10 TEOST-33 test for a GF-2 specification by running at a lower temperature (285°C) but for a  
 longer period of time ie 24 hours on an 8 g sample of oil. The test is set to measure deposits  
 produced on a heated rod or in the oil itself (filtered residue) and it was expected to match  
 the currently given GF-3 specification limit of 40 mg of deposit. The results are tabulated in  
 Table 8 below:

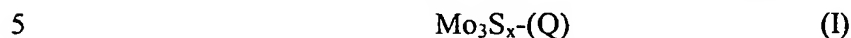
15

**TABLE 8**

Components	Type	Blend	
		5W-30	5W-30
120X (wt %)	Baseoil	81.51	80.51
DI (wt %)	Free of friction modifier	8.29	8.29
PDN5203	Mo-trimer	-	1.00
Paratone® 8451	VI improver	10.00	10.00
Paraflow® 390	Pour point depressant	0.20	0.20
<b>MHT-2 TEOST Test</b>			
Filter wt (mg)		5.2	0.9
Rod wt (mg)		70	26.4
Total wt (mg)		75.2	27.3

## Claims :

1. A lubricating oil composition comprising a base stock and an antioxidant comprising an oil soluble trinuclear organomolybdenum compound of the generic formula:



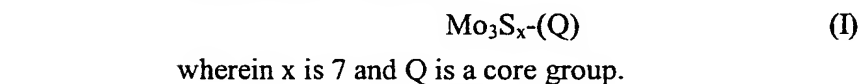
wherein x is from 4 to 10, preferably 7, and Q is a core group, which may be a ligand, and at least one other compound selected from a phenolic and an aminic compound characterised in that the base stock has a kinematic viscosity at 100°C (KV<sub>100</sub>) from about 2 cSt to 20 cSt ( $2 \times 10^{-6}$  to  $20 \times 10^{-6}$  m<sup>2</sup>/sec) and a saturates content of at least 85%.

10

2. A composition according to Claim 1 wherein the basestock is a Group II or Group III base stock which may be a natural or synthetic lubricating oil having a KV<sub>100</sub> of 2-12 cSt.

15

3. A composition according to any one of the preceding Claims wherein the trinuclear molybdenum compounds are of formula (I)



20

4. A composition according to any one of the preceding Claims wherein the core group Q is a ligand capable of rendering the organomolybdenum compound of formula (I) oil soluble and ensuring that said molybdenum compound is substantially charge neutral.

25

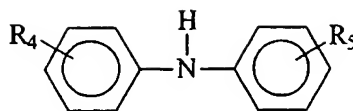
5. A composition according to any one of the preceding Claims wherein the phenolic compound is a hindered phenol.

6. A composition according to any one of the preceding Claims wherein the aminic compound is selected from one or more of diaryl amines, aryl naphthyl amines and alkyl derivatives of diaryl amines and the aryl naphthyl amines of the formulae (VII) or (VIII) below wherein each of R<sub>4</sub> and R<sub>5</sub> is a hydrogen atom or represents the same or different alkyl groups from 1-8 carbon atoms.

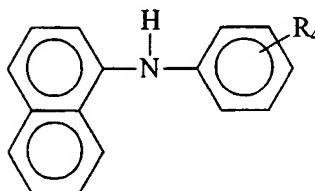
30



(VII)



(VIII)



7. A composition according to any one of the preceding Claims wherein the antioxidant which comprises the trinuclear organomolybdenum compound and at least one other compound selected from a phenolic and/or an aminic compound form a minor component of the total lubricant composition.
8. A composition according to any one of the preceding Claims wherein the antioxidant which comprises the trinuclear organomolybdenum compound and an aminic compound form a minor component of the total lubricant composition.
9. A composition according to any one of the preceding Claims wherein the trinuclear organomolybdenum compound is present in said composition in an amount of about 0.05 to about 5.00 wt % of the total composition.
10. A composition according to any one of the preceding Claims wherein the amount of phenolic and/or aminic compounds present in said composition is about 0.10 to about 3.0 wt % of the total composition.
11. A method of stabilizing a lubricant composition against oxidative degradation, said composition comprising a basestock which has a kinematic viscosity at 100°C (KV<sub>100</sub>) from about 2 cSt to 20 cSt ( $2 \times 10^{-6}$  to  $20 \times 10^{-6}$  m<sup>2</sup>/sec) and a saturates content of at least 85% said method comprising adding to the basestock an effective amount of an antioxidant comprising an oil soluble trinuclear organomolybdenum compound of the generic formula:



wherein x is from 4 to 10, preferably 7, and Q is a core group, which may be a ligand, and at least one other compound selected from a phenolic and an aminic compound.

- 5 12. A method of improving fuel economy of a lubricant composition, said composition comprising a basestock which has a kinematic viscosity at 100°C (KV<sub>100</sub>) from about 2 cSt to 20 cSt ( $2 \times 10^{-6}$  to  $20 \times 10^{-6}$  m<sup>2</sup>/sec) and a saturates content of at least 85% said method comprising adding to the basestock an effective amount of an antioxidant comprising an oil soluble trinuclear organomolybdenum compound of the  
10 generic formula:



wherein x is from 4 to 10, preferably 7, and Q is a core group, which may be a ligand, and at least one other compound selected from a phenolic and an aminic compound.

15

## INTERNATIONAL SEARCH REPORT

National Application No

PCT/US 01/09730

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10M169/04 C10M159/18 //C10N10:12,30:04,30:06,30:10,40:25

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 01 30948 A (INFINEUM INTERNAT LTD) 3 May 2001 (2001-05-03) page 1, line 30 -page 3, line 20 page 9, line 12 -page 10, line 24 page 14 page 16, line 1 -page 16, line 11 page 19 page 20 --- -/-	1-4,7-10



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&\* document member of the same patent family

Date of the actual completion of the international search

3 August 2001

Date of mailing of the international search report

09/08/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Perakis, N

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 01/09730

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 47629 A (INFINEUM UK LTD ;INFINEUM USA LP (US)) 23 September 1999 (1999-09-23) abstract page 1, line 4 -page 1, line 7 page 6, line 18 -page 7, line 20 page 9 page 14, line 12 -page 14, line 20 example 1 claims 1,4,9 ---	1-12
X	WO 98 26030 A (EXXON RESEARCH ENGINEERING CO ;EXXON CHEMICAL PATENTS INC (US)) 18 June 1998 (1998-06-18) abstract page 2 -page 3 page 8 -page 15 examples 5,6 examples 27,28 claims 4-7,10,14,15,18,20-22 ---	1-12
A	US 5 906 968 A (ARUNASALAM VELAUTHA-CUMARAN ET AL) 25 May 1999 (1999-05-25) -----	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/09730

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0130948 A	03-05-2001	US 6074993 A	13-06-2000
WO 9947629 A	23-09-1999	US 6143701 A	07-11-2000
		AU 3032999 A	11-10-1999
		BR 9908737 A	21-11-2000
		EP 1062308 A	27-12-2000
WO 9826030 A	18-06-1998	US 5888945 A	30-03-1999
		AU 729795 B	08-02-2001
		AU 6002498 A	03-07-1998
		BR 9713710 A	24-10-2000
		EP 0960178 A	01-12-1999
		US 6232276 B	15-05-2001
		US 6010987 A	04-01-2000
US 5906968 A	25-05-1999	AU 2160799 A	05-07-1999
		WO 9931113 A	24-06-1999
		EP 1040115 A	04-10-2000
		US 6110878 A	29-08-2000

**THIS PAGE BLANK (USPTO.**

CORRECTED VERSION

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
23 August 2001 (23.08.2001)

PCT

(10) International Publication Number  
WO 01/60959 A1

(51) International Patent Classification<sup>7</sup>: C10M 169/04,  
159/18 // C10N 10:12, 30:04, 30:06, 30:10, 40:25

Robert [CA/US]; Mont Laurel, NJ 08801 (US). WOOL-  
LEY, Paul, S. [GB/GB]; 33 Equine Way, Newbury,  
Berkshire RG14 7XB (GB).

(21) International Application Number: PCT/US01/09730

(74) Agent: MULLER, W., G.; ExxonMobil Chemical Europe  
Inc., P.O. Box 105, B-1830 Machelen (BE).

(22) International Filing Date: 8 February 2001 (08.02.2001)

(81) Designated States (*national*): AU, BR, CA, JP, SG, US.

(25) Filing Language: English

(84) Designated States (*regional*): European patent (AT, BE,  
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,  
NL, PT, SE, TR).

(26) Publication Language: English

(30) Priority Data:  
0003388.6 14 February 2000 (14.02.2000) GB

Published:  
— with international search report

(71) Applicant (*for all designated States except US*): EXXON-  
MOBIL RESEARCH AND ENGINEERING COM-  
PANY [US/US]; 1545 Route 22 East, Clinton Township,  
Annandale, NJ 08801 (US).

(48) Date of publication of this corrected version:  
6 December 2001

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): GAO, Jason  
[CA/US]; 535 Walnut Lane, Swarthmore, PA 19081 (US).  
MAY, Christopher, John [CA/CA]; 1571 Bove Court,  
Samia, Ontario N7S 4A7 (CA). TORKELOSON, Jeffrey,

(15) Information about Correction:  
see PCT Gazette No. 49/2001 of 6 December 2001, Section  
II

*For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.*



WO 01/60959 A1

(54) Title: ANTIOXIDANT ADDITIVE COMPOSITION FOR LUBRICATING OILS

(57) Abstract: This invention relates to a lubricating oil composition comprising a base stock and an antioxidant comprising an oil soluble trinuclear organomolybdenum compound of the generic formula (I):  $\text{Mo}_3\text{S}_x\text{-(Q)}$  wherein x is from 4 to 10 and Q is a core group, which may be a ligand, and at least one other compound selected from a phenolic and an aminic compound wherein the basestock has a kinematic viscosity at 100 °C ( $\text{KV}_{100}$ ) from about 2 cSt to 20 eSt ( $2 \times 10^{-6}$  to  $20 \times 10^{-6} \text{ m}^2/\text{sec}$ ) and a saturates content of at least 85 %. The composition has a high oxidation stability, reduced deposit formation and is capable of giving rise to a good fuel economy improvement.

**THIS PAGE BLANK (USPTO.**